

PCT

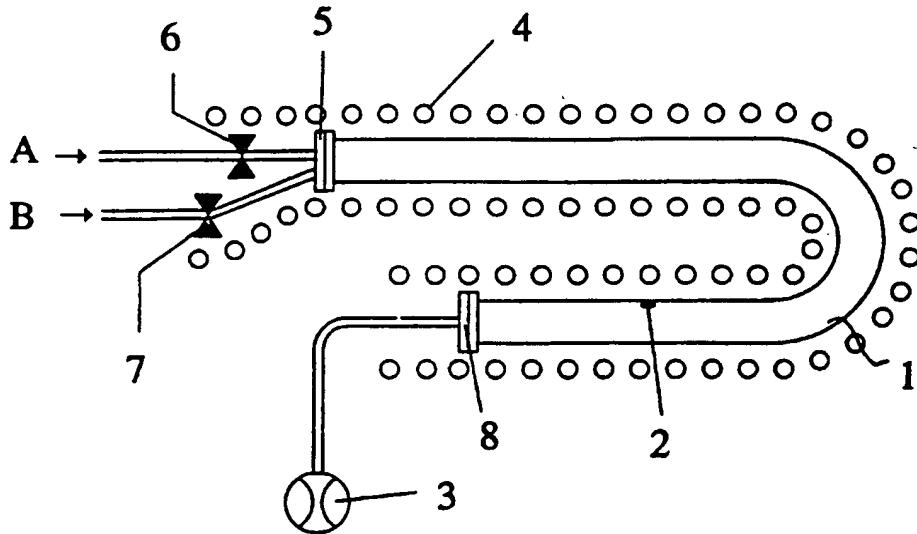
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C23C 16/04, 16/44, C30B 25/02	A1	(11) International Publication Number: WO 99/29924 (43) International Publication Date: 17 June 1999 (17.06.99)
(21) International Application Number: PCT/FI98/00955		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
(22) International Filing Date: 9 December 1998 (09.12.98)		
(30) Priority Data: 974472 9 December 1997 (09.12.97) FI		
(71) Applicant (for all designated States except US): NESTE OYJ [FI/FI]; Keilaniemi, FIN-02150 Espoo (FI).		
(72) Inventors; and		
(75) Inventors/Applicants (for US only): SUNTOLA, Tuomo [FI/FI]; Vasamatie 25, FIN-02630 Espoo (FI). LESKELÄ, Markku [FI/FI]; Rauduntie 19 D, FIN-02130 Espoo (FI). RITALA, Mikko [FI/FI]; Antreantie 8 B, FIN-02140 Espoo (FI).		Published With international search report. In English translation (filed in Finnish).
(74) Agents: LAINE, Seppo et al.; Seppo Laine Oy, Itämerenkatu 3 B, FIN-00180 Helsinki (FI).		

(54) Title: METHOD FOR COATING INNER SURFACES OF EQUIPMENT



(57) Abstract

This invention concerns a method for coating the inner surfaces of equipment with a layer of material. According to the invention, of the inner space of the equipment limited by the surfaces to be coated is at least partly closed, to said inner space pulses of at least two different reagents in gaseous phase are fed alternately and repeatedly and a layer of material is grown on the surfaces of the inner space according to ALE-technique by exposing the surfaces to the alternating surface reactions of the reagents. With the aid of the invention it is possible to coat pipes and tanks of desired size without using a separate growing equipment.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		

Method for coating inner surfaces of equipment

The present invention relates to the coating of surfaces. In particular, the invention

5 concerns a method for coating the inner surfaces of equipment with a layer of material according to the preamble of claim 1.

The purpose of coating surfaces is to improve or alter the properties of a material, such as the resistance of corrosion and stress, optical or electrical properties or to reduce friction.

10 The material of the coating is selected by the application it is used for and by the material that is to be coated. The coatings may be metals or ceramics depending on the desired property and on the operating conditions. The motive for coating pipes and the inner surfaces of tanks is most often to improve the resistance of corrosion (both chemical and abrasive corrosion) and, occasionally, to reduce friction.

15 Recently, new methods for coating the inner surfaces of pipes have been developed. Of the physical methods (PVD), may be mentioned ion beam sputtering, in which method a conical target material is moved inside the pipe and a sputtering ion beam is directed into the pipe from the other end of the pipe (W. Ensinger: Surface and Coatings Technology, 86/87 (1996) 438; A. Schumacher, G. Frech, G.K. Wolf: Surface and Coatings Technology, 99 (1997) 258). The method has been applied only to growing some metal- and nitride films, and the measures of the pipe that is coated, including its length and diameter, have been only in the order of centimetres.

25 The other PVD-method is based on the use of plasma in the coating process (Surfcoat). With this method it is at this moment possible to coat pipes that have a diameter of 30 mm and a length of 1000 mm. The quality of the coating is approximately similar to the quality of normal plasma coating. Evaporation is one of the most common PVD -techniques.

30 The defect of all the PVD-methods is the limited size of the pipe that can be coated. The bending places are still a clear problem and the quality of the film is, even at its best, only of the quality that can be achieved on a plane substrate.

The inner surfaces of the pipes can also be coated electrochemically, especially with electroless plating (auto catalyst) technique. According to the method, the metal is reduced from solution chemically. This technique can be applied only to certain materials (metals and certain compounds). The advantage of this method is that the conformality may be 5 good, as is evidenced by an example of a Cu -coating with USLI-technology (V.M. Dubin et al. Journal of the Electrochemical Society 144 (1997) 898).

The chemical vapour deposition (CVD) is a known method for growing conformal thin films. Satisfactory results are obtained, when the chemical reaction functions as desired. In 10 prior art CVD is also suggested to be used in coating the inner surfaces of pipe (L. Pointier et al., Electrochemical Society Proceedings 97-25 (1997) 425). In general, the studied solutions comprise the coating of metal pipes with a ceramic coating and the lengths of the pipes have been in the order of a few centimetres. A known example of using CVD 15 technique for coating inner surfaces of pipes is the manufacture of the inmost layer of the fiber, which is made by growing a layer inside a billet tube, in the manufacture of optical fiber. According to CVD method the reactant flowing through the tube is attached to the surface of the tube by heating a narrow area at a time. The hot area is thus moved forward along the tube while the tube is rotated. After growing a layer, the tube is collapsed and, thereafter, the actual pulling of the fiber can take place (T. Li: Optical Fiber 20 Communications, part 1, Fiber fabrication, Academic Press, Orlando 1985, p. 363).

The defect of the methods described above is their lack of possibility to coat atomically accurate complicated (bended), large pipings or vessels. Likewise, each method is appropriate only for producing a film with certain constitution.

25 The atomically controlled production of material is known as Atomic Layer Epitaxy (ALE) method, US patent publication 4 085 430. The production of material according to the method is performed by placing the body to be coated in a reactor where conditions enabling alternating surface reactions between the body to be coated and each necessary 30 gaseous reagent are created [T. Suntola: Thin Solid Films 216 (1992) 84]. Typical bodies to be coated are wafers and glass substrates for the manufacture of, among other things, flat displays.

The size and shape of the ALE-reactor determine typically the size and shape of the bodies that can be coated. Since in most of the reaction solutions protective gas is used for carrying the reagents and for separating individual reaction steps, the shape of the body to be coated should be such that enables a sufficiently homogenous gas flow in the reactor.

5

The objective of the present invention is to remove the problems of the prior art and to provide an entirely new solution by using alternating surface reactions.

The invention is based on the idea that the inner surface of the equipment is coated by

10 making the inner space of the body a closed, controlled gas space, the gas content of which is controlled with valve gears that are used for closing the inner space of the body. With the help of valve gears the interior of the body is alternately filled with the reagent gases required, the partial pressures of which are sufficient to saturate the reactive points of the surface. In other words, the amount of the gas molecules is as great as, or greater than the

15 amount of the reactive sites. Thus, in each stage the reagent that is fed into the space forms an atomic layer of the material donated by the reagent onto the inner surface of the body. The density of the atomic layer is determined by the density of the reactive sites. The temperature of the inner surfaces of the body is controlled with the help of heating device placed outside the body or by feeding heat-transfer liquid or gas into the body before the

20 coating step.

More specifically, the process according to the invention is characterised by what is stated in the characterising part of claim 1.

25 Considerable advantages are obtained with the aid of the invention. The method is particularly practical for coating the inner surfaces of pipes and piping and different kinds of tanks and facilities that consist of both pipes and tanks. In this invention the ALE-method is used for coating the inner surfaces of pipes and tanks without using separate growing equipment. For this reason, the size of the surface to be coated is not limited, but

30 the method can be used to coat entire process configuration or even the whole piping of a factory. Furthermore, with present invention, the problematic areas, such as the angle parts, can be well coated. Similarly, the films can be grown on non-conductors, for which the electrical methods are known to be inapplicable.

The characteristic features and the advantages of the invention shall become apparent from the following detailed description. In the description, enclosed drawings are referred to. Of these drawings

5 Figure 1 presents, in schematic manner, how the invention can be applied to coating a pipe and

Figure 2 respectively presents the coating of equipment that consists of pipes and tanks.

In present invention, the ALE-technique, known as such, is used for growing corrosion protection films on the inner surfaces of pipes and pipings chemically from the gas phase.

10 In the method according to the invention, the "growing equipment" is the pipe or tank or that kind of process apparatus, that is to be coated and it is connected to the sources from where the gas pulses come. If necessary, the pipes may be heated externally to the

temperature that is required by the growing reaction. The heating may be arranged by conducting heat-conveying medium such as gas or vapour. These heating methods may be

15 connected if necessary. The external heating is of course best suited for heat-conducting constructions, such as metal piping and tanks. The use of internal heating is advantageous in solutions where the heat capacity of the pipe or equipment is rather large, thus maintaining the temperature on the course of the process.

20 The reaction space is thus formed by the piping or tank to be coated which is equipped with an inlet and possibly outlet collar and which is heated to the temperature required by the process. When working with a flow-through equipment, the outlet end of the equipment does not need to be closed. In the method in question, the inner space of the equipment is closed both at the inlet and the outlet end and to the tank is dosed an amount 25 of gaseous reagent that is sufficient for total area coverage.

The actual growing of film is conducted according to the ALE-method (see, e.g., US 4 058 430 and US 4 389 973). According to the ALE-technique, the reagent is attached from the gas phase on the surface of the solid material in conditions where the amount of the reagent

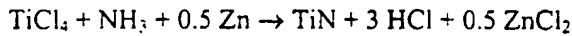
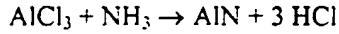
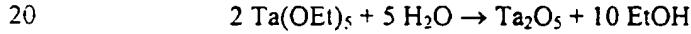
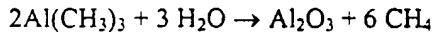
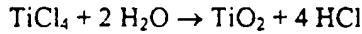
30 attaching to the surface is determined by the surface. The reagents are fed to the equipment alternately and separated from one another with an inert gas pulse. In a breathing equipment a precise dosing of both reagents from layer to layer to accomplish growing is possible. With a precise dosing, a carrier gas is not needed at all. The reagent is attached

from the gas to a surface bond site, with which in this application is meant a site in the inner surface, which is able to react with gaseous reagent.

The films that are grown may of their composition be oxides, nitrides, chalcogenides etc.,

5 in other words, the films may be of any type of those that can be grown with ALE-technique. Typically, however, oxide and nitride films are used in corrosion protection. Similarly, the reagents are the same volatile compounds, which have been used conventionally in ALE-growing, in other words, of metals, volatile inorganic compounds (typically halogenides, metal complexes, such as carboxylates, ketonates, thiocarbamates, 10 amido or imido complexes), metal organic compounds (alkyl compounds, cyclopentadienyl compounds etc.) and in some cases pure metals (e.g., Zn, Cd, Hg). Of non-metals the source compounds to be used for producing oxides are water, hydrogen peroxide, oxygen, ozone, alcohols and for producing nitrides ammonia or organic nitrogen compounds.

15 As examples of used reactions as simplified gross reactions the following may be presented:



The last example shows how the reaction may be enhanced with a third reagent. In the 25 reaction in question, gaseous zinc reduces Ti(IV) to Ti(III) and helps in formation of TiN. The Zn-pulse is given after TiCl₄-pulse. This kind of additional reduction has been proven to be good especially in producing transition element nitrides, where the metal is in a higher oxidation level in the starting compound halogenide than in the product nitride (e.g., M. Ritala, M. Leskelä, E. Rauhala, P. Haussalo, Journal of the Electrochemical society 142 30 (1995) 2731).

One way of improving the endurance of the films is to use multiple film constructions. The ALE-method enables easily the manufacture of different kinds of layers in same process. By growing two different oxides, e.g., Ta₂O₅-HfO₂, Al₂O₃-TiO₂, in turns in layers of

thickness of a couple of nanometres the insulation properties can be improved (the insulation properties correlate also with corrosion properties).

According to the first preferred embodiment presented in Figure 1, the coating of a piping

5 construction is conducted by

- a. emptying the space limited by the inner surface 2 of pipe 1 from gases that possibly disturb the coating reactions with pump 3,
- b. bringing surface 2 to the temperature required for the surface reactions used in the 10 coating process with the aid of heaters 4 placed outside of body 1,
- c. conducting reagent A from valve 6, which is connected to pipe 1 *via* collar 5, to the space at least such an amount that is sufficient for occupying the surface bond sites on surface 2,
- d. removing the possible excess amount of reagent A *via* collar 10 to pump 3,
- 15 e. conducting reagent B *via* valve 9 to the space such an amount that is sufficient for occupying the surface bond sites on surface 2,
- f. removing the possible excess amount of reagent B to pump 3,
- g. repeating steps c..f in cycles so many times that the coating reaches desired thickness.

20 As is apparent from above, the coating of the pipe is conducted mainly in the same manner as the film growing in an ALE-reactor, i.e., the reagents are fed alternately to the equipment and they flow through continuously.

25 In Figure 2 is presented an embodiment of the method for equipment which consists of pipes and tanks. Numbers 11-18 correspond to the respective parts of equipment 1-8 in previous figure. The procedure described above may also be applied to the equipment according to Figure 2 with the difference that the gaseous reagent is dosed to tank 11 in an amount that is sufficient to achieve total coverage of the surface. The inner gas space of the tank is closed by closing valve 19 that is in the pipe between collar 18 and pump 13.

30 Preferably, an excess amount of reagent is dosed to tank 11. The reagent is let to react with the wall of the tank the desired reaction time and, thereafter, the tank is emptied of the gaseous reagent by opening valve 13 leading to pump 13. Thereafter, valve 19 is closed and the next reagent is fed to the tank.

According to an alternative embodiment, in the second step, the surface is brought to the temperature required for the surface reactions used in the coating process with the aid of a heat-transfer liquid or gas led to the space limited by the surface to be coated before the coating steps. If necessary, if the thermal time constant of the body is too small to maintain

5 the temperature of the surface to be coated inside desired temperature range during the whole coating process, the second step is repeated once or more times after the cycle consisting of steps c...f.

According to a third preferred embodiment the removal of excess reagents in steps d and f
10 is enhanced with a flow of protective gas.

According to a fourth preferred embodiment, there are more feeding steps of reagents than the steps c, d and e, f described above. The additional steps are used to ensure the surface reactions of the reagents or to complete them.

15 The following non-limiting example will clarify the invention.

Example 1

Coating of piping

20 The length of the exemplary piping is 100 m, the diameter is 50 mm. Thus the area of the inner surface that is to be coated is $100 \times 0.157 = 15.7 \text{ m}^2$. The volume of the piping is approx. 0.2 m^3 . With a method according to the invention a Al_2O_3 layer with a thickness of 0.2 μm is grown on the inner surface of the piping. As reagent is used (a) trimethyl aluminium and (b) water vapour.

25 Prior to commencing the actual process, the cleanness of the inner surface of the piping is checked and, if necessary, said surface is cleaned by, e.g., conducting suitable solvent through the piping. The piping is dried after possible wet washing with the aid of, e.g., gas flow and heating.

30 In step a the piping is essentially evacuated from air gases and of the gases possibly detaching from the walls of the piping.

In step b the piping is heated externally with the aid of a heating flow set around the piping at 200 °C. Pumping and the flow of protective gas which may accompany pumping is continued during the heating step. Before starting the next steps, it is made sure that the partial pressures of oxygen and water vapour and other gases which may react with

5 reagents A and B are below 10^{-3} mb in the piping. To fasten the proceeding of the reagents in the piping, it is advantageous, if the total pressure of the piping is kept below 1 mb.

In step c reagent A is conducted to the piping in vapour phase at least approx. 0.02 g.

10 In step d the excess amount of reagent A is removed by pumping until the partial pressure of A in the piping is below 10^{-3} mb.

In step e at least approximately 0.005 g reagent B in vapour phase is conducted to the piping.

15

In step f the excess amount of reagent b is removed from the piping by pumping until the partial pressure of B in the piping is below 10^{-3} mb.

The steps c...f are repeated in cycles 2000 times.

20

The time needed for the heating step depends on the heating effect used and on the heat capacity of the piping. In practise, heating and pumping carried out at the same time improves the achieved cleanliness of the surface, thus making it preferable to use several hours or a couple of days for the heating and emptying step. Conducting of the steps c...f

25 takes 10 – 100 seconds, thus, production of a coating with a thickness of 0.2 μ m takes from a couple of hours to a couple of days.

Claims:

1. A method for coating the inner surfaces of equipment with a layer of material, characterized in that

5 - at least a part of the inner space limited by the inner surfaces of equipment is closed,
- to said inner space are alternately and repeatedly fed vapour phase pulses of at least two different reagents, and
- on the surfaces of the inner space is grown a layer of material according to
10 ALE-technique by exposing the surfaces to the alternating surface reactions of the reagents.

2. The method according to claim 1, characterized in that volatile compounds, such as the inorganic compounds of metals, metalorganic compounds or pure metals, water,

15 hydrogen peroxide, oxygen, ozone, alcohols, ammonia or organic nitrogen compounds are used as reagents.

3. The method according to claim 1 or 2, characterized by the combination of the following steps:

20 a. emptying the space limited by the inner surface (2;13) from gases which possibly disturb the coating reactions with pump (3;13),
b. bringing surfaces (2;12) to the temperature required for the surface reactions used in the coating process,
c. feeding the first reagent (A) to the space limited by the surfaces (2;12) at least such
25 an amount that is sufficient for occupying the surface bond sites on surfaces,
d. removing the possible excess amount of the first reagent (A) from said space,
e. feeding the second reagent (B) to the space limited by the surfaces (2;12) at least such an amount that is sufficient for occupying the surface bond sites on surfaces,
f. removing the possible excess amount of the second reagent (B) from said space,
30 and
g. repeating steps c...f in cycles so many times that the coating reaches desired thickness.

4. The method according to claim 3, characterized in that the surface to be coated is brought to the temperature required for the surface reactions used in the coating process with the aid of heaters placed outside the body.
5. The method according to claim 3, characterized in that the surface to be coated is brought to the temperature required for the surface reactions used in the coating process by feeding heat-transfer liquid or gas before the coating steps to the space limited by the surface (2;12) to be coated.
- 10 6. The method according to claim 5, characterized in that heat-transfer liquid or gas is led more than once to the space limited by the surface to be coated (2;12) after the cycle consisting of steps c...f.
- 15 7. The method according to any of claims 3 – 6, characterized in that in steps d and f the removal of excess amounts of reagents (A,B) is made more efficient with the aid of protective gas flow.
- 20 8. The method according to any of claims 3 – 7, characterized in that in addition to first and second reagent, at least one other reagent is added to the space limited by the surface to be coated (2;12), to ensure/complete the surface reactions caused by the first and the second reagent.
- 25 9. The method according to any of the preceding claims, characterized in that to the equipment, an inner space limited by the surfaces to be coated is created by closing the space with the aid of valve gears (6, 7; 16, 17, 19).
- 30 10. The method according to claim 9, characterized in that at least one of the valve gears (6, 7; 16, 17) is used in feeding the reagents, when at least two reagent sources (A, B) are connected to said valve gear.
11. The method according to claim 9 or 10, characterized in that at least one valve gear (18) is used for removing the excess gas.

12. The method according to any of the preceding claims, characterized in that the inner surface of process equipment, such as piping or tank (1,11) is coated.
13. The method according to any of claims 1 – 12, characterized in that with the coating, the stress or corrosion endurance or optical or electrical properties of the inner surface of equipment are improved or friction is decreased.
14. The method according to any of the preceding claims, characterized in that an oxide, nitride and/or chalcogenide layer is grown on the inner surface.

1/1

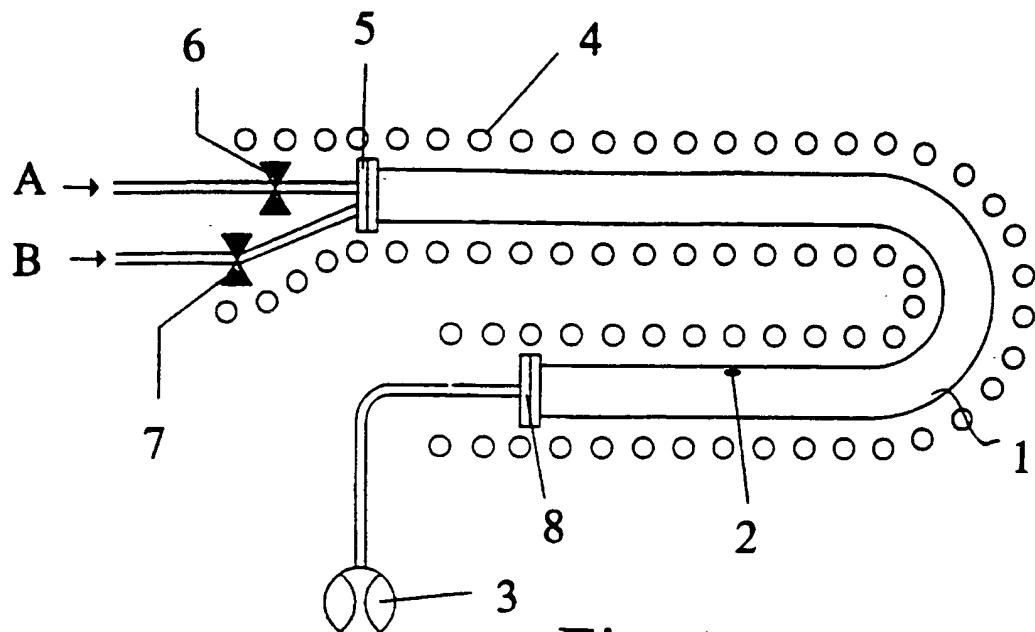


Fig. 1

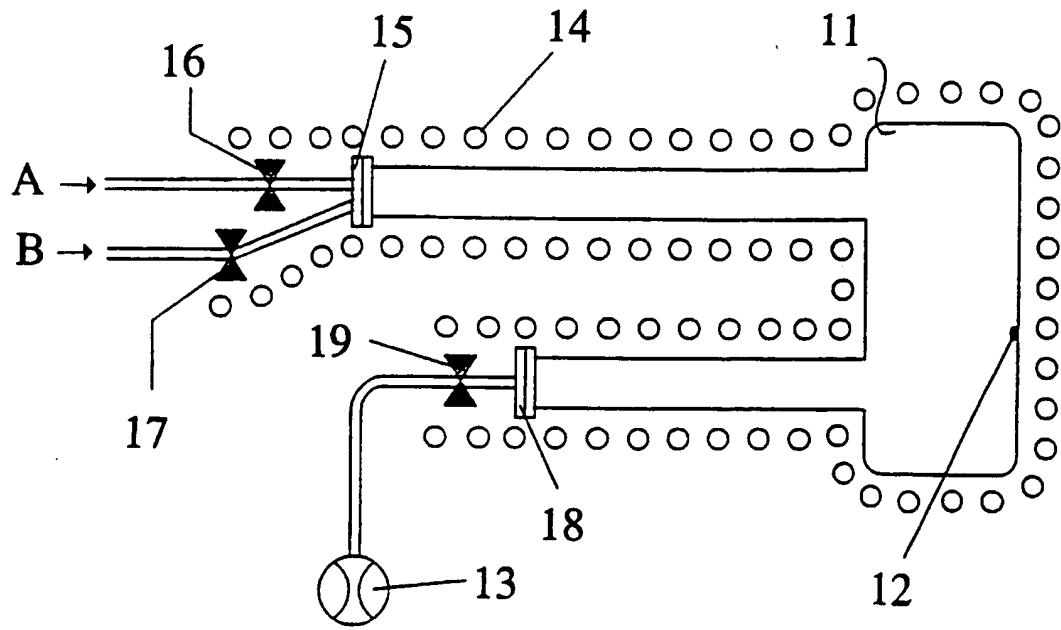


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 98/00955

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C23C 16/04, C23C 16/44, C30B 25/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C23C, C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

QUESTEL: EDOC, WPIL, JAPIO, DIALOG: DIALINDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4975252 A (JUNICHI NISHIZAWA ET AL), 4 December 1990 (04.12.90), column 4, line 48 - line 66; column 5, line 29 - line 43, figure 1 --	1-14
A	EP 0015390 A1 (OY LOHJA AB), 17 Sept 1980 (17.09.80), page 6, line 6 - line 17; page 9, line 10 - line 30, figures 1,8 -----	1-14

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

- "&" document member of the same patent family

Date of the actual completion of the international search

15 March 1999

Date of mailing of the international search report

17 -03- 1999

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. + 46 8 666 02 86

Authorized officer

Bengt Christensson
Telephone No. + 46 8 782 25 00

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/FI 98/00955

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4975252 A	04/12/90	DE 3526888 A,C FR 2582149 A GB 2162207 A,B GB 2200137 A,B GB 2200138 A,B JP 2577542 B JP 61034924 A US 5443033 A JP 2050511 C JP 7066907 B JP 61034925 A JP 2050512 C JP 7066908 B JP 61034926 A	06/02/86 21/11/86 29/01/86 27/07/88 27/07/88 05/02/97 19/02/86 22/08/95 10/05/96 19/07/95 19/02/86 10/05/96 19/07/95 19/02/86
EP 0015390 A1	17/09/80	SE 0015390 T3 AT 15820 T AU 535151 B AU 5578680 A BR 8001087 A CA 1166937 A DK 84680 A DK 157943 B,C FI 57975 B,C IN 152596 A JP 1299997 C JP 55130896 A JP 60021955 B SU 1085510 A US 4413022 A ZA 8000852 A	15/10/85 08/03/84 04/09/80 29/10/80 08/05/84 29/08/80 05/03/90 31/07/80 18/02/84 31/01/86 11/10/80 30/05/85 07/04/84 01/11/83 25/02/81